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(54) Radiation-resistant polycarbonates

Strahlungsbeständige Polycarbonate

Polycarbonates résistants à la radiation

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(56) References cited:
EP-A- 0 303 894 **EP-A- 0 551 608**
US-A- 4 904 717

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DescriptionField of the Invention

5 The subject of this invention are thermoplastic composition as defined in the claims containing an aromatic polycarbonate resin and (i) dialkyl and/or dicycloalkyl monosulfides or polysulfides in an amount of 0.001 to 5 weight %, preferably 0.005 to 1 weight %, in particular 0.01 to 0.8 weight %, each based on 100 weight % of aromatic polycarbonate, and optionally (ii) aliphatic or cycloaliphatic monoalcohols or polyalcohols or their derivatives in an amount of 0.001 to 2 weight %, preferably 0.001 to 1.5 weight %, based on 100 weight % of an aromatic polycarbonate.

SUMMARY OF THE INVENTION

10 The polycarbonate compositions of the invention are stabilized against gamma γ -rays and, therefore, are well suited for medical applications in a multitude of ways, especially for the manufacture of equipment or equipment parts which must be sterilized either before or after use through ionizing radiation, while avoiding the occurrence of excessive yellowing.

BACKGROUND OF THE INVENTION

20 EP-A-303 894 teaches to include organic thioethers together with phenolic antioxidants to stabilise polymers made of unsaturated hydrocarbons, particularly PP, against gamma-rays.

Details of the invention

25 Thermoplastic, aromatic polycarbonates in the sense of the invention are both homopolycarbonates and copolycarbonates; the polycarbonates can be linear or branched by known means.

A portion, up to 80 mol %, preferably between 20 and 50 mol % of the carbonate groups in the appropriate polycarbonates based on the invention can be replaced by aromatic dicarboxylic acid ester groups. Such polycarbonates can contain not only built-in carbonic acid radicals, but also acid radicals of aromatic dicarboxylic acids in the molecular chain, more precisely described as aromatic polyester carbonates. These are referred to in the present application for purposes of simplicity under the generic term of thermoplastic, aromatic polycarbonates.

30 The production of the polycarbonate useful in the context of the invention is known. These are produced from diphenols, carbonic acid derivatives, optionally with chain terminators and branching agents, whereby a part of the carbonic acid derivatives may be replaced by aromatic dicarboxylic acid or derivatives of dicarboxylic acid for the production of the polyester carbonate.

35 Details of polycarbonate production have been specified in hundreds of patent specifications for about 40 years. A few of them are pointed out, for example, in Schnell's Chemistry and Physics of Polycarbonates, Polymer Reviews, Volume 9, Inter-science Publishers, New York, London, Sydney 1964; D. C. PREVORSEK, B. T. DEBONA and Y. KESTEN, "Synthesis of Poly(ester Carbonate) Copolymers" in the Journal of Polymer Science, Polymer Chemistry Edition, Vol. 18, 75-90 (1980); D. Freitag, U. Grigo, P. R. Müller, H. Nonvertue, "Polycarbonates" in the Encyclopedia of Polymer Science and Engineering, Volume 11, Second Edition, 1988, pages 648-718, and finally Drs. U. Grigo, K. Kircher and P. R. Müller "Polycarbonate" in Becker/Braun, Plastics-Handbook, Handbook, Volume 3/1, Polycarbonate, Polyacetals, Polyester, Cellulose Ester, Carl Hanser Verlag München, Wen 1992, pages 117-299.

45 Thermoplastic polycarbonates, including the thermoplastic, aromatic polyester carbonates, have weight average molecular weights M_w (determined by measuring the relative viscosity at 25°C in CH_2Cl_2 and a concentration of 0.5 g per 100 ml CH_2Cl_2) between 12,000 and 120,000, preferably between 18,000 and 80,000 and in particular between 22,000 and 60,000.

50 Diphenols suitable for the production of the polycarbonate to be stabilized in accordance with the invention are hydroquinone, resorcinol, dihydroxydiphenyls, bis-(hydroxyphenyl)-alkanes, bis-(hydroxyphenyl)-cycloalkanes, bis-(hydroxyphenyl)sulfides, bis-(hydroxyphenyl)-ether, bis-(hydroxyphenyl)-ketones, bis-(hydroxyphenyl)-sulfones, bis-(hydroxyphenyl)-sulfoxides, α, α' -bis-(hydroxyphenyl)-diisopropyl benzene, as well as their nucleous alkylated and nucleous halogenated compounds.

55 Preferred diphenols are 4,4'-dihydroxydiphenyl, 2,2-bis-(4-hydroxyphenyl)-propane, 2,4-bis-(4-hydroxyphenyl)-2-methylbutane, 1,1-bis-(4-hydroxyphenyl)-p-diisopropyl benzene, 2,2-bis-(3-methyl-4-hydroxyphenyl)-propane, 2,2-bis-(3-chloro-4-hydroxyphenyl)-propane, bis-(3,5-dimethyl-4-hydroxyphenyl)-methane, 2,2-bis-(3,5-dimethyl-4-hydroxyphenyl)-propane, bis-(3,5-dimethyl-4-hydroxyphenyl)-sulfones, 2,4-bis-(3,5-dimethyl-4-hydroxyphenyl)-2-methylbutane, 1,1-bis-(3,5-dimethyl-4-hydroxyphenyl)-p-diisopropyl benzene, 2,2-bis-(3,5-dichloro-4-hydroxyphenyl)-propane, 2,2-bis-(3,5-dibromo-4-hydroxyphenyl)-propane and 1,1-bis-(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane.

Especially preferred diphenols are 2,2-bis-(4-hydroxy-phenyl)-propane, 2,2-bis-(3,5-dimethyl-4-hydroxyphenyl)-propane, 2,2-bis-(3,5-dichloro-4-hydroxyphenyl)-propane, 2,2-bis-(3,5-dibromo-4-hydroxyphenyl)-propane, 1,1-bis-(4-hydroxyphenyl)-cyclohexane and 1,1-bis-(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane.

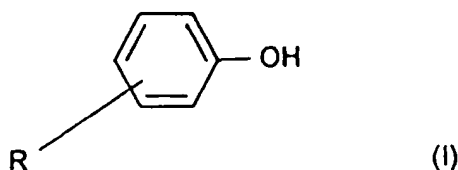
These and other suitable diphenols are described in US-A-3,028,635, 2,999,835, 3,148,172, 2,991,273, 3,271,367, 4,982,014 and 2,999,846; in DE-A-1,570,703, 2,063,050, 2,036,052, 2,211,956, and 3,832,396; FR-A-1,561,518; in the monograph "H. Schnell, Chemistry and Physics of Poly-carbonates, Interscience Publishers, New York 1964", as well as in the JP-A-62039/1986, 62040/1986 and 105550/1986.

In the case of the homopolycarbonates, only one diphenol is used; in the case of the copolycarbonates, several diphenols are used.

Suitable chain terminators are both monophenols and monocarboxylic acids. Suitable monophenols are phenol itself, alkylphenols like cresol, p-tert-butylphenol, p-n-octylphenol, p-iso-octylphenol, p-n-nonylphenol and p-iso-nonylphenol, halogenphenols, such as p-chlorophenol, 2,4-dichlorophenol, p-bromophenol and 2,4,6-tribromophenol.

Suitable monocarboxylic acids are benzoic acid, alkylbenzoic acids and halogenbenzoic acids.

Preferred chain terminators are the phenols of the formula (I)



wherein

R is a branched or unbranched C₈-alkyl and/or C₉-alkyl radicals.

The quantity of chain terminator to be used is between 0.5 and 10 mol %, based on moles of the diphenols. The addition of the chain terminators can be made before, during, or after the phosgenation.

Suitable branching agents suitable for polycarbonate are the well known compounds having a functionality of three or more, in particular, those with three or more phenolic OH-groups.

Suitable branching agents include phloroglucinol, 4,6-dimethyl-2,4,6-tri-(4-hydroxyphenyl)-heptene-2, 4,6-dimethyl-2,4,6-tri-(4-hydroxyphenyl)-heptane, 1,3,5-tri-(4-hydroxyphenyl)-benzene, 1,1,1-tri(4-hydroxyphenyl)-ethane, tri-(4-hydroxyphenyl)-phenylmethane, 2,2-bis-[4,4-bis-(4-hydroxyphenyl)-cyclohexyl]-propane, 2,4-bis-(4-hydroxyphenyl-isopropyl)-phenol, 2,6-bis-(2-hydroxy-5'-methylbenzyl)-4-methylphenol, 2-(4-hydroxyphenyl)-2-(2,4-dihydroxyphenyl)-propane, hexa-(4-(4-hydroxyphenyl-isopropyl)-phenyl)-ortho-terephthalic acid ester, tetra-(4-hydroxyphenyl)-methane, tetra-(4-(4-hydroxyphenyl-isopropyl)-phenoxy)-methane and 1,4-bis-(4',4'-dihydroxytriphenyl)-methyl)-benzene, as well as 2,4-dihydroxybenzoic acid, trimesic acid, cyanuric chloride and 3,3-bis-(3-methyl-4-hydroxyphenyl)-2-oxo-2,3-dihydroindol.

The quantity of branching agent to be used is between 0.05 and 2 mol %, based on the moles of the diphenols used in each case.

Branching agents can either be included with the diphenols and the chain terminators in an alkaline aqueous phase, or can be added or dissolved in an organic solvent prior to phosgenation.

All these measures for the production of polycarbonates are known to the expert.

Suitable aromatic dicarboxylic acids for the production of polyester carbonate are, for example, orthophthalic acid, terephthalic acid, isophthalic acid, tert-butylisophthalic acid, 3,3'-diphenyldicarboxylic acid, 4,4'-diphenyldicarboxylic acid, 4,4'-benzophenone dicarboxylic acid, 3,4-benzophenone dicarboxylic acid, 4,4'-diphenylether dicarboxylic acid, 4,4'-diphenylsulfone dicarboxylic acid, 2,2-bis-(4-carboxy-phenyl)-propane, trimethyl-3-phenylindane-4,5'-dicarboxylic acid.

From the aromatic dicarboxylic acids, terephthalic acid and/or isophthalic acid are preferably used.

Derivatives of the dicarboxylic acids are dicarboxylic acid dihalogenides, and the dicarboxylic acid dialkylesters, especially the dicarboxylic acid dichlorides and the dicarboxylic acid dimethyl esters.

The application of carbonate groups through the aromatic dicarboxylic acid ester groups is basically stoichiometric, and also quantitative, such that the molecular ratio of the reaction partners is also reflected in the finished polyester carbonate. The incorporation of the aromatic dicarboxylic acid ester groups can be made either in statistical or blocked operation.

Preferred methods of producing polycarbonate suitable in the present context, including the polyester carbonates, are the well known interfacial surface polycondensation process and the melt transesterification process.

In the first case, phosgene serves preferably as the carbonic acid derivative; in the second case, diphenylcar-

bonate.

Catalysts, solvents, preparation, reaction conditions, etc. are in both cases conventional and well known.

The dialkyl- and dicycloalkyl- monosulfides and polysulfides are those of the formula (II)



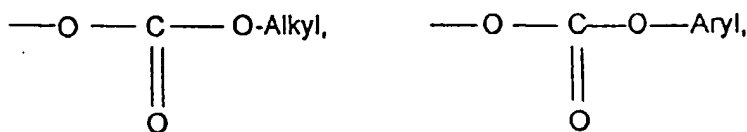
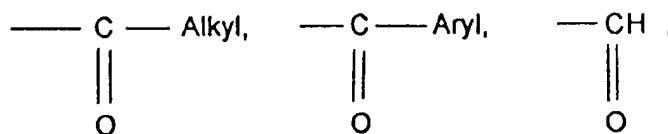
wherein,

R^1 and R^2 independently denote C_1 - C_{40} -alkyl or C_3 - C_{15} -cycloalkyl radicals, which can either be unsubstituted or substituted.

Preferred alkyl radicals are linear chains such as $C_{12}H_{25}$, $C_{16}H_{33}$, $C_{17}H_{35}$ and $C_{18}H_{37}$, and branched such as t - $C_{12}H_{25}$; preferred cycloalkyl radicals are cyclopentyl, cyclohexyl, and cycloheptyl.

The index "n" has a value from 2 to 4.

Suitable substituent groups on the alkyl radicals and the cycloalkyl radicals are -SH, C_1 - C_5 -alkoxy, C_1 - C_5 -alkylthio, phenoxy, phenylthio, -COOH, alkoxycarbonyl, aryloxycarbonyl,



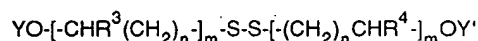
- SO_3H , - SO_3 -alkyl, - SO_3 -aryl, - SO_2H , - SO_2 -alkyl, SO_2 -aryl, SOH, -SO-alkyl, -SO-aryl and for the alkyl radicals R^1 and R^2 cycloalkyl and aryl and for the cycloalkyl radicals R^1 and R^2 alkyl and aryl, whereby these last alkyl-substitutes could be saturated or unsaturated.

Preferred compounds (II) are those where "n" equals 2:



where R^1 and R^2 independently are C_1 - C_{40} alkyl or hydroxyalkyl radicals, more preferably C_2 - C_{30} alkyl or $C_{2,30}$ hydroxyalkyl radicals, especially C_{12-18} alkyl or hydroxyalkyl radicals are especially preferred. 2-hydroxyethyl disulfide is an example of a suitable compound.

In an additionally preferred embodiment of the invention the disulfide conforms to the formula



where Y and Y' independently one of the other denote a hydrogen atom or a C_1 - C_{30} alkyl or acyl radical, a pyranlyl or silyl group, preferably a hydrogen atom, a C_1 - C_5 alkyl or pyranlyl radical, m is 1-70 preferably 4-50 and n is 1-4, preferably 1 and R^3 and R^4 independently denote hydrogen, C_1 - C_{22} alkyl, cycloalkyl, aryl, alkylaryl, or cycloalkyl-aryl radicals, preferably C_1 - C_5 alkyl radicals.

The compounds of the formula (II) are known from the literature and may be produced based on a literature-known process (see, Houben-Weyl, "Methods in Organic Chemistry", Volume E 11, "Organic Sulfur Compounds", Georg Thieme, Publisher, Stuttgart-New York, 1985).

Examples of compounds of the formula (II) are dicyclohexyldisulfide, $C_{12}H_{25}$ -SS- $C_{12}H_{25}$, t - $C_{12}H_{25}$ -SS- t - $C_{12}H_{25}$, $C_{16}H_{33}$ -SS- $C_{16}H_{33}$, $C_{17}H_{35}$ -SS- $C_{17}H_{35}$ and $C_{18}H_{37}$ -SS- $C_{18}H_{37}$.

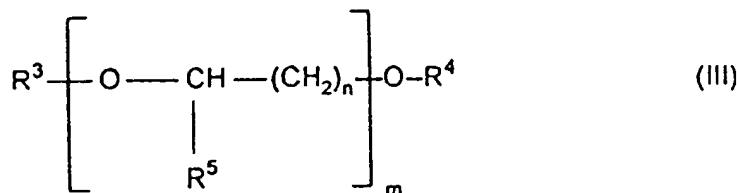
The aliphatic or cycloaliphatic monoalcohols or polyalcohols suitable as additives are preferably C_1 - C_{20} -monoal-

cohols, aliphatic C₂-C₂₀-dialcohols, aliphatic C₃-C₂₀-trialcohols and aliphatic C₄-C₂₀-tetraalcohols, cycloaliphatic C₃-C₁₂-monoalcohols, and cycloaliphatic C₃-C₁₂-dialcohols.

These monoalcohols and polyalcohols are known from the literature (see, for example, Houben-Weyl, "Methods of Organic Chemistry", Volume 6/1a/1, "Alcohols I, Volume 6/1a/2, "Alcohols II" and Volume 6/1b, "Alcohols III", Georg Thieme, Publisher, Stuttgart-New York, 1979, 1980 and 1984).

Preferred monoalcohols are dodecanol, hexadecanol-(1), hexadecanol-(2), stearylalcohol, octadecanol and eicosanol.

Preferred polyalcohols are diols, triols, tetraols, pentaols and hexaols, especially diols of the formula (III)



wherein, the following are

R³=R⁴=H; R⁵, H or C₁-C₄-alkyl; n a whole number between 1 and 36, and m a whole number between 1 and 1500, preferably between 2 and 1200 and in particular between 3 and 1000.

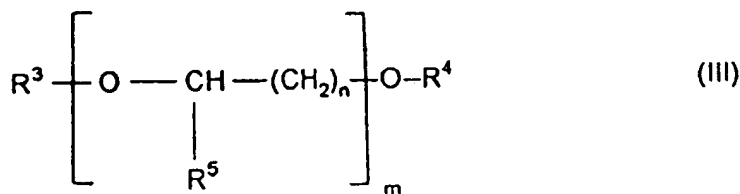
Examples for it are, ethylene glycol, 1,2-propane diol, 1,3-propane diol, 1,2-butane diol, 1,3-butane diol, 1,4-butane diol, 2,3-butane diol, 1,2-pentane diol, 1,5-pentane diol, 2,4-pentane diol, 1,2-hexane diol, 1,6-hexane diol, 3-methyl-1,5-pentane diol, 2,5-hexane diol, 1,2-cyclohexane diol, 1,4-cyclohexane diol, cyclohexyl-1,4-dimethanol, 2-methyl-2,4-pentane diol, 1,8-octane diol, 1,10-decane diol, 1,2-undecane diol, 1,2-dodecane diol, 1,12-dodecane diol, 1,2-hexadecane diol, 1,2,5-pentane triol, 1,2,3-hexane triol, 1,2,6-hexane triol, 2-(hydroxymethyl)-2-methyl-1,3-propane diol and 2,3,4,5,6,7,-octane hexaol.

Derivatives of monoalcohols or polyalcohols based on the invention are their ethers, carboxylic esters, acetals, alkylcarbonates, epoxides, urethanes, phosphate esters, phosphonate esters, phosphoric esters, phosphonic esters, and siloxanes.

These derivatives are known from the literature and may be prepared by methods known from the literature (See the respective volumes of Houben-Weyl, "Methods of Organic Chemistry", Georg Thieme Publishers).

Preferred derivatives are ethers, carboxylic acid esters, acetals and alkylcarbonates of the monoalcohols or polyalcohols; examples for it are diethylene glycol, diethylene glycoldiethylether, dipropylene-glycol, tripropylene glycol, 1,3-diethoxy-2-propanol, 3,3'-oxibis-(1,2-propane diol), 2,2'-oxibisbutane, the alkylesters of the undecanoic acid, dodecanoic acid, hexadecanoic acid, stearic acid and dodecanoic acid, glycerin monostearate, glycerin distearate, glycerin tristearate, 1,1-bis-(2,3-dioctadecanyloxy-propyloxy)-hexadecane, 2,2-dicyclohexyloxypropane, acetoxy-(4-(2-tetrahydropyranyloxy)-pentyloxy)-methane, acetoxy-dodecyloxymethane, acetoxy-(3-(2-methyl-1,3-dioxolane-2-yl)-propyloxy)-methane, ethylenecarbonate, dimethylcarbonate, diethylcarbonate, dipropylcarbonate, diisopropylcarbonate and dineopentylcarbonate.

Especially well suited are such of the formula (III)



wherein

R³ and R⁴ independently are C₁ to C₃₀-alkyl, and may be either branched or unbranched, or acyl, silyl and/or pyranlyl,

R⁵ denotes H or C₁ to C₄-alkyl,

n denotes a whole number from 1 to 36, and

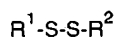
m denotes a whole number from 1 to 1500, preferably from 2 to 1200 and in particular from 3 to 1000.

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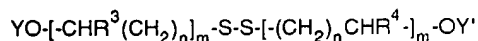
The compounds of the formula (III) may preferably have a molecular weight of from 106 g/mol to 100,000 g/mol, especially preferred from 150 g/mol to 12000 g/mol, and in particular from 500 g/mol to 10,000 g/mol.

Preferred is a thermoplastic molding composition comprising a polycarbonate resin and a stabilizing agent which includes

(i) 0.1 to 1.5% of an aliphatic disulfide conforming to the formula



where R^1 and R^2 independently are C_{2-30} alkyl or hydroxyalkyl radicals, or to the formula

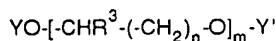


where Y and Y' independently one of the other denote a hydrogen atom or a C_{1-30} alkyl or acyl radical, a pyranlyl or silyl group,

m is 1 to 70,

n is 1 to 4, and R^3 and R^4 independently denote hydrogen, C_{1-22} -alkyl, cycloalkyl, aryl, alkylaryl or cycloalkyl-aryl radicals, and optionally

(ii) 0.1 to 1.5% of a polyether polyol conforming to the formula

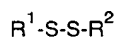


where

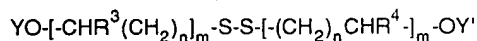
n, m, Y, Y', and R^3 are as defined above, said percents being relative to the weight of said composition.

Especially preferred is a thermoplastic molding composition comprising a polycarbonate resin and a stabilizing agent which includes

(i) 0.1 to 1.5 % of an aliphatic disulfide conforming to the formula



or to the formula



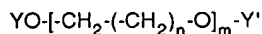
where Y and Y' independently denote pyranlyl, acyl or silyl groups,

m is 1 to 70,

n is 1 to 4, and R^1 and R^2 independently denote C_{2-30} alkyl or hydroxy alkyl radicals,

R^3 and R^4 independently denote hydrogen, and

(ii) 0.1 to 1.5 % of a polyether polyol having a number average molecular weight of about 2000 conforming to the formula



where Y and Y' both denote pyranlyl radicals, said percents being relative to the weight of said composition.

The addition of the sulfides and optionally monoalcohols or polyalcohols or their derivatives to the polycarbonate

may be either simultaneous or sequential at temperatures between 260 and 380°C through the melting process of the polycarbonate, or through the solution of the polycarbonate in known solvents such as CH_2Cl_2 and/or chlorobenzene, and subsequent evaporation of the solvents in known ways.

A process for production of the polycarbonate to be stabilized is characterized by the fact that the dialkyl or/and dicycloalkyl monosulfides or polysulfides, and optionally the aliphatic or cycloaliphatic monoalcohols or polyalcohols or their derivatives are mixed with polycarbonates at temperatures between 260 and 380°C in mixing vessels that are normally used, as for example, a kneading or extrusion machinery, or that the dialkyl or/and dicycloalkyl monosulfides or polysulfides, and optionally the aliphatic or cycloaliphatic monoalcohols or polyalcohols or their derivatives are dissolved with polycarbonates in known solvents, such as CH_2Cl_2 and/or chlorobenzene, and the mixtures of the dialkyl- or/and dicycloalkyl monosulfides or polysulfides, and optionally the aliphatic or cycloaliphatic monoalcohols or polyalcohols or their derivatives obtained in this way are isolated with polycarbonates through subsequent evaporation of the solvents in known ways.

Suitable equipment for the production of polycarbonates to be stabilized according to the invention for the case of addition to the polycarbonate by melting is a kneader or extruder, and in the case of addition to the polycarbonate by solution vessel is a mixing agitated vessel.

The irradiation of polycarbonate molded parts with ionized radiation, such as γ -rays or electronic rays is in order to sterilize objects, such as dialysators for blood exchange, one-way syringes, etc. prior to their medical use. Damage always occurs, thereby, for example, in the form of a yellowing of the polycondensate. In order to minimize this damage or to avoid it, the polycondensate must be stabilized prior to irradiation.

The stabilization of aromatic polycarbonates and/or aromatic copolycarbonates and/or aromatic polyestercarbonate against ionizing radiation, such as γ -rays and/or electronic rays is known from the literature. In US-A-4,624,972 polycarbonate mixtures with aromatic polycarboxylic acid esters are specified, which are to a certain extent resistant against γ -radiation. The EP-A-152,012 and EP-A-228,525 specify mixtures of polycarbonates with non-polymeric compounds which show strong oxidation action and/or high turnover of reactants, such as, OH-radicals or solvating electrons that are formed by ionizing radiation. US-A-4,451,641 describes copolyesters, which are stabilized to a certain extent through dimeric acids or dimeric glycols against damage by γ -radiation.

It was surprising that the compounds of the formula (II), especially in combination with monoalcohols or polyalcohols or their derivatives can exert an excellent stabilizing effect on the polycarbonates or polyesterarbonates against the influence of γ -rays, such that the polycondensate to be stabilized clearly yellows less strongly in each case than the stabilizer systems already known from the present state of the art, which can be shown through determination of the difference in the yellowness index.

The polycarbonate stabilized against γ -rays based on the invention can still contain the normal additives such as thermo-stabilizers, UV-absorbers, flowing agents, demolding agents, softeners, antistatics, flame retardants and/or dyes, and for special applications also fillers, for example, glass fibers or glass spheres. The addition is made to the usual quantities of polycarbonate under normal conditions and machines. The addition can be made before, during, or after the stabilization based on the invention through sulfides and eventually alcohols or their derivatives.

The processing of the polycarbonates stabilized according to the invention to any molded parts, especially medical equipment, done using on known injection-molding and extrusion machines.

The application of parts molded from polycarbonates stabilized according to the invention can, aside from the medical field, also be used in the areas with foodstuffs contact, as packaging material of any form, as well as in all other application areas where polycarbonates are normally used.

The invention is further illustrated but is not intended to be limited by the following examples in which all parts and percentages are by weight unless otherwise specified.

EXAMPLES

The relative solvent viscosities (η_{rl}) of the polycondensates were determined at 25°C. For this, 0.500 g of the condensates each was dissolved in 100 ml dichloromethane.

Production of the polycarbonate mixtures with stabilizers

The examples of the mixtures of polycarbonates with different stabilizers for the γ -irradiation listed in the following table were produced on a dual shaft extruder at 300°C mass temperature. Color sample coupons (Size: 60 mm x 40 mm x 4 mm) were produced at a 300°C processing temperature from the mixtures obtained. These were sterilized with 3Mrad γ -irradiation.

The combinations of the mixtures and the test results are summarized in the following table.

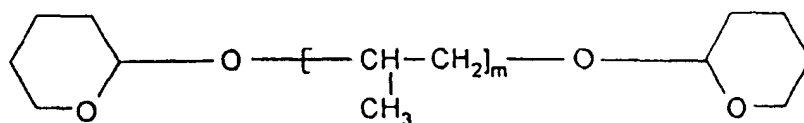
Results

Sample/ Additive	(C ₁₈ H ₃₇ S) ₂ (weight %)	(C ₁₇ H ₃₇ S) ₂ (weight %)	Polypropylene glycol of the formula (III) with R ³ =R ⁴ =R ⁵ =H M _w = 2000 (weight %)	Polycarbonate based on bis- phenol A re. 1.289 (weight %)	Y.I
1	0.1		0.75	100	11.8
2	0.5		0.75	100	5.0
3		0.5	0.75	100	8.0
Comparison				100	24
Comparison			0.75	100	13

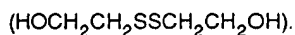
Y.I = Yellowness Index

Y.I = Y.I 10 days after γ -irradiation - Y.I before γ -irradiation.Experimental II.

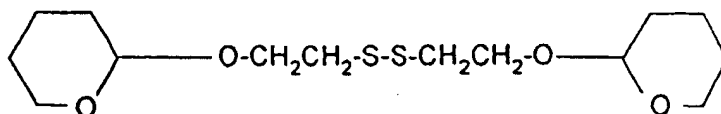
Molding compositions in accordance with the invention have been prepared and their properties determined. In the preparation of the compositions the resin used was a homopolycarbonate based on bisphenol-A having a melt flow rate of about 15 gm/10 min. The additives noted below were incorporated in the polycarbonate composition in the indicated amounts. Example 1 contained the stabilizer of the invention exemplified by mixture of a polyether polyol conforming to



10 having a number average molecular weight of about 2000 and the aliphatic disulfide was 2-hydroxyethyl disulfide



15 In Example 2, only polyether polyol was used. Example 3 demonstrates the performance of polycarbonate resin without any stabilizers and Example 4 contains the polyether polyol and an aromatic disulfide- the subject of the above mentioned copending patent application Serial Number 07/891,875. Example 5 contained the polyether polyol and 2-pyranylethyl disulfide conforming to



25 and Example 6 contained 2-pyranylethyl disulfide only as the stabilizer.

The polycarbonate and additives were tumble blended together and then extruded on a ZSK-30 twin screw extruder at a melt temperature of about 270°C. The extruded strands were cooled, chopped into pellets and the pellets then molded at about 280°C into chips measuring 0.100 inch in thickness (about 0.25 cm.)

30 The chips were subjected to gamma radiation at doses of 3 mrad. The yellowness index (YI) of the as molded and as irradiated chips were determined in accordance with ASTM D 1925. The measurements were taken approximately 24 hours after exposure to the radiation.

The table below show the effect of the radiation on the several compositions.

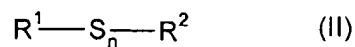
5		6	-	-	-	0.1	10.0	14.1	4.1
10		5	0.5	-	-	0.1	5.9	11.5	5.5
15		4	0.5	-	0.5	-	4.39	8.7	4.3
20		3*	-	-	-	-	5.04	24.5	19.5
25		2*	1.0	-	-	-	2.92	14.1	11.2
30	1	0.5	0.5	-	-	-	9.43	10.73	1.3
35	additive, % polyether polyol	0.5	0.5	-	-	-	9.43	10.73	1.3
40	2-hydroxyethyl disulfide	0.5	-	-	-	-	9.43	10.73	1.3
	diphenyl disulfide	-	-	-	-	-	9.43	10.73	1.3
	2-pyranyl ethyl disulfide	-	-	-	-	-	9.43	10.73	1.3
	Yellowness index								
	Pre-radiation	9.43	2.92	5.04	4.39	5.9	10.0		
	after exposure	10.73	14.1	24.5	8.7	11.5	14.1		
	difference in yellowness index	1.3	11.2	19.5	4.3	5.5	4.1		
	* comparative								

The results show the efficacy of the stabilizer of the present invention set in comparison to relevant compositions.

Claims

1. A thermoplastic molding composition comprising an aromatic polycarbonate and

(i) sulfides conforming to formula (II)



wherein R¹ and R² independently denote dicycloalkyl radicals or C₃-C₁₅-cycloalkyl radicals and wherein n is a whole number between 2 and 4 in an amount of 0.001 to 5 weight %, and optionally

(ii) aliphatic or cycloaliphatic monoalcohols or polyalcohols or the derivatives of the monoalcohols or the polyalcohols selected from the group of their ether, carboxylic acid ester, acetal, alkylcarbonate, epoxide, urethane, phosphate ester, phosphonate ester, phosphoric ester, phosphonic ester and siloxane, in an amount of 0.001 to 2 weight %,

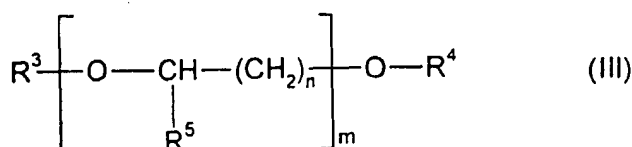
said percents being relative to 100 weight % of aromatic polycarbonate.

2. The composition of Claim 1 wherein said R¹ and R² independently are substituted.

3. The composition of Claim 1 wherein said aliphatic alcohols are selected from the group consisting of aliphatic C₁-C₂₀-monoalcohols, aliphatic C₂-C₂₀-dialcohols, aliphatic C₃-C₂₀-trialcohols and aliphatic C₄-C₂₀-tetraalcohols.

4. The composition of Claim 1 wherein said cycloaliphatic alcohols are C₃-C₁₂-monoalcohols or C₃-C₁₂-dialcohols.

5. The composition of Claim 1 wherein the aliphatic alcohols or their derivatives conform to the formula (III), wherein



R³ and R⁴ independently denote H, C₁- to C₃₀-alkyl, acyl, silyl or pyranlyl,

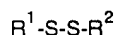
R⁵ denotes H or C₁ to C₄-alkyl,

n is a whole number between 1 and 36, and

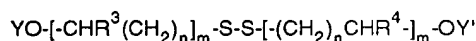
m is a whole number between 1 and 1500.

6. A thermoplastic molding composition of Claim 1 comprising a polycarbonate resin and a stabilizing agent which includes

(i) 0.1 to 1.5 % of an aliphatic disulfide conforming to the formula



where R¹ and R² independently are C₂₋₃₀ alkyl or hydroxyalkyl radicals, or to the formula

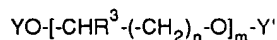


where Y and Y' independently one of the other denote a hydrogen atom or a C₁₋₃₀ alkyl or acyl radical, a pyranlyl or silyl group,

m is 1 to 70,

n is 1 to 4, and R³ and R⁴ independently denote hydrogen, C₁₋₂₂-alkyl, cycloalkyl, aryl, alkylaryl or cycloalkyl-aryl radicals, and optionally

(II) 0.1 to 1.5 % of a polyether polyol conforming to



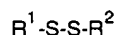
where

n, m, Y, Y', and R³ are as defined above,

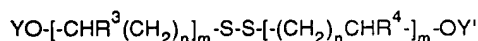
said percents being relative to the weight of said composition.

7. A thermoplastic molding composition of Claim 1 comprising a polycarbonate resin and a stabilizing agent which includes

(i) 0.1 to 1.5 % of an aliphatic disulfide conforming to the formula



or to the formula



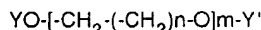
where Y and Y' independently denote pyranlyl, acyl or silyl groups,

m is 1 to 70,

n is 1 to 4, and R¹ and R² independently denote C₂₋₃₀ alkyl or hydroxy alkyl radicals,

R³ and R⁴ independently denote hydrogen, and

(ii) 0.1 to 1.5 % of a polyether polyol having a number average molecular weight of about 2000 conforming to the formula



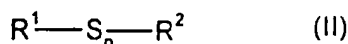
where Y and Y' both denote pyranlyl radicals,

said percents being relative to the weight of said composition.

Patentansprüche

1. Thermoplastische Formmassen-Zusammensetzung, umfassend ein aromatisches Polycarbonat und

(i) Sulfide gemäß der Formel (II)



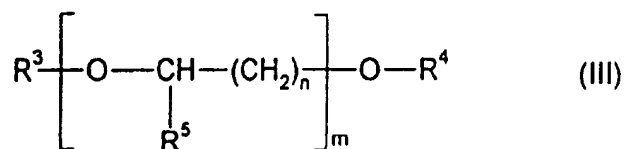
worin R¹ und R² unabhängig voneinander C₁-C₄₀-Alkyl-Reste oder C₃-C₁₅-Cycloalkyl-Reste bedeuten und n eine ganze Zahl von 2 bis 4 ist, in einer Menge von 0,001 bis 5 Gew.-%, und gegebenenfalls

(ii) aliphatische oder cycloaliphatische Monoalkohole oder Polyalkohole oder die Derivate der Monoalkohole oder der Polyalkohole, die aus der Gruppe ihrer Ether, Carbonsäureester, Acetale, Alkylcarbonate, Epoxide, Urethane, Phosphatester, Phosphonatester, Phosphorsäureester, Phosphonsäureester und Siloxane ausgewählt sind, in einer Menge von 0,001 bis 2 Gew.-%,

wobei die prozentualen Angaben sich auf 100 Gew.-% des aromatischen Polycarbonats beziehen.

2. Zusammensetzung gemäß Anspruch 1, worin R¹ und R² unabhängig voneinander substituiert sind.
3. Zusammensetzung gemäß Anspruch 1, worin die aliphatischen Alkohole aus der aus aliphatischen C₁-C₂₀-Monoalkoholen, aliphatischen C₂-C₂₀-Dialkoholen, aliphatischen C₃-C₂₀-Trialkoholen und aliphatischen C₄-C₂₀-Tetraalkoholen bestehenden Gruppe ausgewählt sind.
4. Zusammensetzung gemäß Anspruch 1, worin die cycloaliphatischen Alkohole C₃-C₁₂-Monoalkohole oder C₃-C₁₂-Dialkohole sind.

5. Zusammensetzung gemäß Anspruch 1, worin die aliphatischen Alkohole oder deren Derivate der Formel (III)



entsprechen, worin

R^3 und R^4 unabhängig voneinander H, C_1 - C_{30} -Alkyl, Acyl, Silyl oder Pyranyl bedeuten,

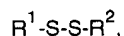
R^5 H oder C_1 - C_4 -Alkyl bedeutet,

n eine ganze Zahl von 1 bis 36 ist, und

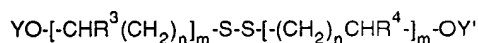
m eine ganze Zahl von 1 bis 1500 ist.

6. Thermoplastische Formmassen-Zusammensetzung gemäß Anspruch 1, umfassend ein Polycarbonatharz und ein Stabilisierungsmittel, welches einschließt

(i) 0,1 bis 1,5 % eines aliphatischen Disulfids gemäß der Formel



worin R^1 und R^2 unabhängig voneinander C_{2-30} -Alkyl- oder Hydroxyalkyl-Reste sind, oder der Formel

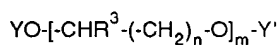


worin Y und Y' unabhängig voneinander ein Wasserstoffatom oder einen C_{1-30} -Alkyl- oder -Acylrest, eine Pyranyl- oder eine Silylgruppe bedeuten,

m 1 bis 70 ist,

n 1 bis 4 ist, und R^3 und R^4 unabhängig voneinander Wasserstoff, C_{1-22} -Alkyl-, Cycloalkyl-, Aryl-, Alkylaryl- oder Cycloalkylaryl-Reste bedeuten, und gegebenenfalls

(ii) 0,1 bis 1,5 % eines Polyetherpolyols gemäß



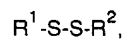
worin

n , m , Y, Y' und R^3 wie oben definiert sind,

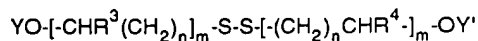
wobei die prozentualen Angaben sich auf das Gewicht der Zusammensetzung beziehen.

7. Thermoplastische Formmassen-Zusammensetzung gemäß Anspruch 1, umfassend ein Polycarbonatharz und ein Stabilisierungsmittel, welches einschließt

(i) 0,1 bis 1,5 % eines aliphatischen Disulfids gemäß Formel



oder der Formel



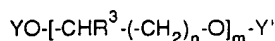
worin Y und Y' unabhängig voneinander Pyranyl-, Acyl- oder Silylgruppen bedeuten,

m 1 bis 70 ist

n 1 bis 4 ist, und R¹ und R² unabhängig voneinander C₂₋₃₀-Alkyl- oder -Hydroxyalkylreste bedeuten,

R³ und R⁴ unabhängig voneinander Wasserstoff bedeuten, und

(ii) 0,1 bis 1,5 % eines Polyetherpolyols eines Molmassen-Zahlenmittels von etwa 2000 gemäß der Formel



worin

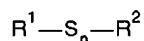
Y und Y' jeweils Pyranylreste bedeuten,

wobei die prozentualen Angaben sich auf das Gewicht der Zusammensetzung beziehen.

Revendications

1. Composition de moulage thermoplastique comprenant un polycarbonate aromatique et

(i) des sulfures conformes à la formule (II)



dans laquelle R¹ et R² représentent indépendamment des radicaux alkyle en C₁-C₄₀ ou des radicaux cycloalkyle en C₃-C₁₅ et dans laquelle n est un nombre entier compris entre 2 et 4 dans une quantité de 0,001 à 5 % en poids, et facultativement

(ii) des monoalcools ou des polyalcools aliphatiques ou cycloaliphatiques ou les dérivés des monoalcools ou des polyalcools choisis parmi leurs éthers, esters d'acides carboxyliques, acétals, carbonates d'alkyle, époxydes, uréthane, ester de phosphate, ester de phosphonate, ester phosphorique, ester phosphonique et siloxane, dans une quantité de 0,001 à 2 % en poids,

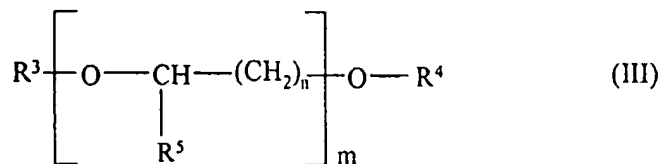
lesdits pourcentages étant rapportés à 100 % en poids de polycarbonate aromatique.

2. Composition selon la revendication 1, dans laquelle lesdits R¹ et R² sont indépendamment substitués.

3. Composition selon la revendication 1, dans laquelle lesdits alcools aliphatiques sont choisis parmi les monoalcools aliphatiques en C₁-C₂₀, les dialcools aliphatiques en C₂-C₂₀, les trialcools aliphatiques en C₃-C₂₀ et les tétrialcools aliphatiques en C₄-C₂₀.

4. Composition selon la revendication 1, dans laquelle lesdits alcools cycloaliphatiques sont des monoalcools en C₃-C₁₂ ou des dialcools en C₃-C₁₂.

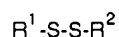
5. Composition selon la revendication 1, dans laquelle les alcools aliphatiques ou leurs dérivés sont conformes à la formule (III), dans laquelle



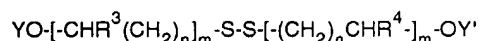
R³ et R⁴ représentent indépendamment H, un groupe alkyle en C₁-C₃₀, acyle, silyle ou pyrannyle,
 R⁵ représente H ou un groupe alkyle en C₁-C₄,
 n est un nombre entier compris entre 1 et 36, et
 m est un nombre entier compris entre 1 et 1 500.

6. Composition de moulage thermoplastique selon la revendication 1, comprenant une résine de polycarbonate et un agent stabilisant qui comprend

(i) de 0,1 à 1,5 % d'un disulfure aliphatique conforme à la formule

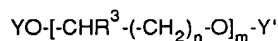


dans laquelle R¹ et R² représentent indépendamment des radicaux alkyle ou hydroxyalkyle en C₂-C₃₀ ou à la formule



dans laquelle Y et Y' représentent indépendamment un atome d'hydrogène ou un radical alkyle ou acyle en C₁-C₃₀, un groupe pyrannyle ou silyle,
 m est compris entre 1 et 70,
 n est compris entre 1 et 4, et R³ et R⁴ représentent indépendamment l'hydrogène, des radicaux alkyle, cycloalkyle, aryle, alkylaryle ou cycloalkylaryle en C₁-C₂₂, et facultativement

(ii) de 0,1 à 1,5 % d'un polyétherpolyol conforme à



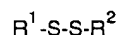
dans laquelle

n, m, Y, Y' et R³ sont comme définis ci-dessus,

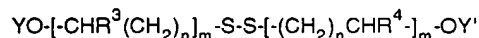
lesdits pourcentages étant rapportés au poids de ladite composition.

7. Composition de moulage thermoplastique selon la revendication 1, comprenant une résine de polycarbonate et un agent stabilisant qui comprend

(i) de 0,1 à 1,5 % d'un disulfure aliphatique conforme à la formule



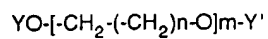
ou à la formule



dans laquelle Y et Y' représentent indépendamment des groupes pyrannyle, acyle ou silyle,
 m est compris entre 1 et 70,
 n est compris entre 1 et 4 et R¹ et R² représentent indépendamment des radicaux alkyle ou hydroxyalkyle en C₂-C₃₀,
 R³ et R⁴ représentent indépendamment l'hydrogène, et

(ii) de 0,1 à 1,5 % d'un polyétherpolyol ayant un poids moléculaire moyen en nombre d'environ 2 000 conforme à la formule

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dans laquelle Y et Y' représentent tous deux des radicaux pyranyle,
lesdits pourcentages étant rapportés au poids de ladite composition.

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